

## THE MUTUAL INFLUENCE OF HYDROXYL AND CARBOXYL AND SOME RELATED GROUPS IN THE ORTHO POSITION

A STUDY OF THE ABSORPTION SPECTRA OF PHENOL, O-CRESOL, O-HYDROXY-BENZYL ALCOHOL, SALICYLIC ACID AND ITS METHYL ESTER, METHYL ETHER OF SALICYLIC ACID AND ITS METHYL ESTER, BENZYL ALCOHOL, BENZYL ACETATE, BENZYL METHYL ETHER, BENZYL CHLORIDE, AND METHYL BENZOATE

By H. D. GIBBS<sup>1</sup> and D. S. PRATT

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Five text figures

The following investigation was undertaken with the view of throwing some light upon the behavior of the compounds which exist in solution during the saponification of methyl salicylate described in the previous paper.<sup>2</sup>

If it be true that the strengths of carboxylic acids are determined by the reactivity of the carboxylic  $>C=O$  group, it should be possible to compare spectroscopically certain analogous acids which show ultra-violet absorption bands. Baly and Schaefer<sup>3</sup> state:

There are thus two influences at work which determine the affinity of the carbonyl group in carboxylic acids, namely, (1) the nature of the adjacent carbon atom, and (2) the condition of the hydroxylic oxygen.

It is to be expected that these influences would change the relative position and persistence of ultra-violet absorption bands, and that a study of a series of closely related compounds in which they are varied, both collectively and separately, would result in a clearer understanding of the chemical and physical behavior of the compounds in solution.

The astonishingly great difference between the saponification rates of methyl salicylate and its sodium salt (6.63 and 0.161, respectively) must be due to a decreased activity of the carbonyl which in this case is attributed to a change in the equilibrium of forces between this group and the hydroxyl group in the ortho position.

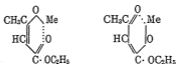
<sup>1</sup> Associate professor of chemistry, University of the Philippines.

<sup>2</sup> Gibbs, Williams, and Galajikian, *This Journal*, Sec. A (1913), 8, 1.

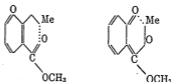
<sup>3</sup> *Journ. Chem. Soc. London* (1908), 93, 1814.

The analogies existing between methyl salicylate and acetoacetic ether are very striking. The chemical relationships have been pointed out by Freer,<sup>4</sup> and determinations of the affinity constants of the acids and the hydrolysis constants of their sodium salts show the former to be of the magnitude  $10^{-11}$  and the latter 0.001 in each case.

The expressions suggested by Hantzsch<sup>5</sup> for the valence isom-



erism in the *aci*-salt in explanation of the absorption band in acetoacetic ether can be applied to methyl salicylate, the corresponding form showing the conjugated linking being:



There is no doubt that methyl salicylate in the presence of alkali behaves very differently from the other phenolic compounds discussed in this paper.

Phenol, *o*-cresol, salicylate acid, and *o*-hydroxybenzyl alcohol in the presence of alkali show a reduction in the persistence of the characteristic absorption band (discussed later), while acetoacetic ether shows no band in the absence of alkali, but develops a characteristic band which increases in persistence with the increasing concentration of alkali salt. Methyl salicylate shows no appreciable change in the persistence of its band with alkali, the effect of increasing concentration of the latter being to shift the band toward the red. If the intramolecular vibration producing this band is to be attributed to the conjugated linking as above represented, it is clear that an excess of alkali has

<sup>4</sup> *Am. Chem. Journ.* (1892), 14, 407.

<sup>5</sup> *Ber. d. deutschen chem. Ges.* (1910), 43, 3053.

a beneficial rather than a prejudicial action. The effect of the alkali is to reduce the phenolic condition, which we will show can be practically eliminated.

This is actually the case in phenol, *o*-cresol, *o*-hydroxybenzyl alcohol, and sodium salicylate. The primary effect of the alkali upon salicylic acid is the formation of the sodium salt, and this is manifested in the absorption spectrum by a shift of the band toward the shorter wave length, a position nearer the characteristic band of phenol.

It is evident that the carboxylic C=O group has not the effect in the di-sodium salt of salicylic acid that it has in the sodium salt of the ester.

The above representation for sodium methyl salicylate indicates that the free affinities of this compound are so bound that in effect its equilibrium more closely resembles that of an ether than of an ester. By this assumption the greatly decreased rate of saponification of sodium methyl salicylate is capable of explanation. Salicylic acid, on the other hand, shows no similar behavior in the presence of alkalies, and presents no corresponding analogies to acetoacetic ether, although the absorption spectra of the free acid and ester are identical. When methyl is employed instead of sodium to replace the hydroxylic hydrogen of methyl salicylate forming the methyl ether of methyl salicylate, the equilibrium is disturbed in a different manner due to the fixation of the labile hydrogen atom, and this is manifested by a shift in the absorption band toward the shorter wave lengths and a decrease in its persistence, indicating decreased activity. This decreased activity cannot be attributed to the phenol portion of the molecule, for the absorption spectrum of phenol is not altered in this way by its change to anisole, but is due to the reduction of the influence upon the  $>C=O$  group.

The strength of salicylic acid is diminished by the change of the hydroxyl group to methoxyl. This is shown in the absorption spectra of these compounds by a decided shift in the absorption band of the former toward the shorter wave lengths. The absorption bands of neither of these compounds are altered by the change of the carbonyl group to its methyl ester. It is evident that the strength of the acid is affected by any neighboring group which will influence the potential activity of the  $>C=O$  group of the carboxyl. The absorption spectra of salicylic acid, methyl ether of salicylic acid, and benzoic acid indicate the strength of these acids to be in the order named, a fact which is in accord with their affinity constants.

The rates of saponification of the methyl esters of the above-mentioned acids and the affinity constants of these acids are tabulated as follows:

Acid.	Rate of saponification of the methyl ester.	Affinity constant.*
Salicylic acid	6.36	0.104
Methyl ether of salicylic acid	<sup>b</sup> 2.03- <sup>c</sup> 2.60	0.0081
Benzoic acid	<sup>b</sup> 4.53- <sup>c</sup> 5.41	0.0067

\* The affinity constants are taken from Derick, *Journ. Am. Chem. Soc.* (1912), 34, 78; Lueder, "Affinitätsmessungen an schwachen Säuren und Basen," *Sammlung chem. u. chem.-tech. Vorträge* (1909), 14, 1; and Ostwald, *Zeitschr. f. physik. Chem.* (1889), 3, 241.

<sup>b</sup> Calculated for reaction of the first order in nonhomogeneous solution.

<sup>c</sup> Calculated for reaction of the second order in homogeneous solution.

These values show that the affinity constants are not in the same order as the saponification constants. Similar irregularities are shown in the values as given for propionic, butyric, and isobutyric acids.

Acid.	Rate of saponification of the ethyl-ester.*	Affinity constant.*
Propionic	2.186	0.00145
Butyric	1.702	0.00175
Isobutyric	1.731	0.00159

\* Values taken from Walker, *Introduction to Physical Chemistry*. London (1910), 163 and 235.

Since the affinity constants of benzoic acid and the methyl ether of salicylic acid lie so close together, and we are at this time most concerned with these two acids, we have redetermined their constants and find that there is no question concerning their relative values. The results are as follows:

The specific conductivity of the water was  $1.19 \cdot 10^{-6}$  at 25°.

TABLE I.—Benzoic acid.  $\alpha_{\infty} = 387$ .

$\phi/1000$ .	$\Delta$	$100\alpha$	$K = 100k$
64	21.48	6.07	0.0061
128	32.93	8.51	0.0062
256	45.39	11.93	0.0062
512	63.09	16.31	0.0062
1.024	81.80	21.65	0.0058
	$K = 0.0061$		

This value agrees with that found by Jones and others<sup>6</sup> when their figures are recalculated in terms of the Kohlrausch units.

<sup>6</sup> *Pub. Carnegie Inst. Wash.* (1912), 170, 116.

TABLE II.—Methyl ether of salicylic acid.  $\alpha_{\infty} = 387$ .

$\phi/1000$ .	A.	100 $\alpha$ .	$K=100k$ .
32	18.85	4.74	0.0073
64	26.30	6.79	0.0077
128	36.81	9.61	0.0078
256	50.77	13.12	0.0077
512	68.46	17.95	0.0078
1,024	95.90	24.55	0.0078
	$K=0.0077$		

This value agrees with that found by Ostwald<sup>7</sup> when his figures are calculated with the Kohlrausch units. If the above values are correctly given, it is evident that the affinity constants of acids are not necessarily measures of the rates of saponification of similar esters of the acids. At the present time sufficient data are not available to explain these anomalies.

Our method of approaching this problem has included a study of the hydroxyl group of phenol and its conversion in part and almost wholly into its sodium salt, a study of benzoic acid and of benzyl derivatives in which the  $>C=O$  has been replaced by  $>CH_2$ , and finally of various ortho combinations of these groups, as found in *o*-cresol, *o*-hydroxybenzyl alcohol, *o*-hydroxybenzoic acid, its sodium salts, methyl ether, and the methyl ester of this ether.

## PHENOL. FIG. 1

The absorption spectrum of phenol has been investigated by Hartley and Huntington;<sup>8</sup> Hartley, Dobie and Lauder;<sup>9</sup> and by Baly and Ewbank.<sup>10</sup> The last authors observed a shift in the absorption band in the presence of 4 equivalents of alkali, a condition which Baly and Desh<sup>11</sup> found in other compounds to be indicative of enol-keto tautomerism.

We have photographed this compound in neutral and acid alcohol solution and in the presence of 0.1, 1, 5, and 500 equivalents of sodium ethoxide, and have found that with the increase in the concentration of the sodium salt of phenol and corresponding decrease of free phenol, the absorption band becomes more

<sup>7</sup> *Zeitschr. f. physik. Chem.* (1889), 3, 266.<sup>8</sup> *Phil. Trans. Roy. Soc. London* (1879), 170, 270.<sup>9</sup> *Journ. Chem. Soc. London* (1902), 81, 929.<sup>10</sup> *Ibid.* (1905), 87, 1347.<sup>11</sup> *Ibid.* (1904), 85, 1029; (1905), 87, 766.

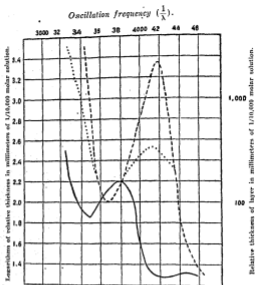


FIG. 1.—Dash curve=phenol.

Dot curve=phenol with 1/10 equivalent of sodium ethoxide.

Full curve=phenol with 5 equivalents of sodium ethoxide.

shallow, is shifted slightly toward the red, and gives every indication of disappearing entirely were all of the phenol in the form of the sodium salt.

The relative proportion of the phenol and sodium phenolate in water solution is obtained from the equation<sup>12</sup>  $\frac{ne}{d} = 0.85 \times 10^{-4}$  in which  $n$ ,  $e$ , and  $d$  are the concentration of the free base, phenol, and sodium salt, respectively. With 5 equivalents of alkali, approximately 98 per cent of the phenol is in the form of the sodium salt. We have not determined this hydrolysis constant in alcohol, but do not believe it to be very different. Under these conditions, the band characteristic of enol-keto tautomerism has diminished to a fraction of its original persistence, and a shallow band in the benzene region of the spectrum has made its appearance. The latter band also makes its

<sup>12</sup> Walker, Introduction to Physical Chemistry. London (1910), 336.

appearance in the presence of 1 equivalent of alkali. It is evident that the intramolecular vibrations of sodium phenolate more nearly approach those of the benzene ring. In fig. 1 the curve with 0.1 equivalent of alkali is plotted from dilution log. 3.5 to log. 2.3 which is the range obtained with 0.01 molar concentration. It is obvious that a dilution of this solution will change the value of  $d$ , so that this curve could not be farther continued with accuracy by this method.

The curve obtained with 1 equivalent of alkali is not plotted in fig. 1 since it falls between the curves of 0.1 and 5 equivalents. Similarly, that with 500 equivalents is omitted since it lies near that with 5 equivalents, but shows a further decrease in persistence of the band. The curve obtained in alcohol saturated with hydrogen chloride follows the curve of neutral phenol, except that the persistence of the transmission band at  $1/\lambda=4180$  is reduced from log. 3.34 to log. 2.82. It is thus seen that acids and alkalies have a somewhat similar effect in reducing the persistence of the absorption band of phenol, which is to be interpreted as producing a more stable molecule.

To test the validity of this assumption, we have exposed to the sunlight tubes of phenol and phenol dissolved in a large excess of a concentrated solution of sodium hydroxide, and find that the former colors in a few hours while the latter fails to show any coloration after weeks of exposure. Sodium phenolate in solution is colored rapidly, but, in the presence of an enormous excess of alkali, the hydrolysis and also the ionization are at a minimum, and we probably have the stable form  $C_6H_5ONa$ . If it be granted that the oxidation of phenol is capable of explanation by reason of the transformation



the two hydrogen atoms being oxidized with the formation of quinone, then it is readily seen that sodium phenolate will resist this transformation since the sodium atom has greater affinity for the oxygen than for the carbon.

#### O-CRESOL. FIG. 2

The absorption spectrum of *o*-cresol has been investigated by Hartley<sup>12</sup> and by Baly and Ewbank. The latter authors observed the shift in the absorption band toward the red, which takes place in the presence of alkalies.

<sup>12</sup> *Journ. Chem. Soc. London* (1888), 53, 641.

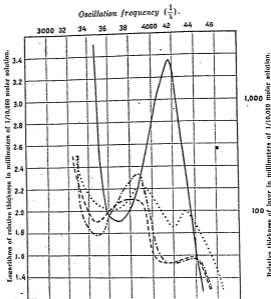


FIG. 2.—Full curve=*o*-cresol in alcohol.  
 Dot curve=*o*-cresol with 1 equivalent of sodium ethoxide.  
 Dash curve=*o*-cresol with 5 equivalents of sodium ethoxide.  
 Dash and dot curve=*o*-cresol in aqueous solution with 5  
 equivalents of sodium hydroxide.

The curves for *o*-cresol in alcohol and in the presence of alkali as shown by Hantzsch<sup>14</sup> cannot be correctly attributed to this compound. It is probable that acetoacetic ether was photographed instead of *o*-cresol, since the curves correspond with his data for the former compound. We have photographed *o*-cresol in alcohol solution and in the presence of 1 and 5 equivalents of sodium ethoxide, and in water solution in the presence of 5 equivalents of alkali. It is to be noted that an absorption band in the benzene region makes its appearance in the presence of alkali, a fact not noted by previous investigators. This band corresponds to that observed with phenol in the presence of alkalies, but appears at slightly greater concentrations.

<sup>14</sup> *Ber. d. deutschen chem. Ges.* (1910), 43, 3071.

The persistence of the band heading at  $1/\lambda=3480$  is much greater in alkaline aqueous solutions than in the corresponding alcohol solutions, a condition which points to the conclusion that the hydrolysis of the sodium salt is greater in aqueous than in alcoholic solutions.

O-HYDROXYBENZYL ALCOHOL. FIG. 3

This compound was photographed in neutral alcohol solution and also in the presence of 5 equivalents of alkali. See dot and dash curve and dot curve, fig. 3. The conditions existing in phenol and *o*-cresol are also found in this compound. The portion of the curve for 5 equivalents of alkali lying below  $\log. 1.7$  was obtained by photographing a 1/1000 molar solution. Since this concentration was obtained by diluting a 1/100 molar solution,

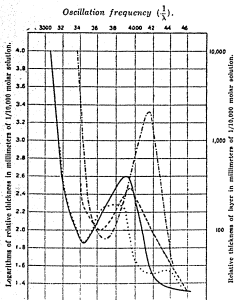


FIG. 3.—Dot and dash curve=*o*-hydroxybenzyl alcohol.  
 Dot curve=*o*-hydroxybenzyl alcohol with 5 equivalents of sodium ethoxide.  
 Full curve=methyl ether of salicylic acid and methyl ether of methyl salicylate.  
 Dash curve=methyl ether of salicylic acid with 5 equivalents of sodium methoxide.

it is clear that the degree of hydrolysis must be different. The two portions of the curve do not quite join, but the variation is so slight that it is not shown in the chart.

METHYL ETHER OF SALICYLIC ACID, AND THE METHYL ETHER OF  
METHYL SALICYLATE. FIG. 3

The methyl ether of salicylic acid may be obtained easily and with a good yield by the following method. One hundred grams of salicylic acid and 70 grams of sodium hydroxide are dissolved in 300 cubic centimeters of water. This concentration of alkali converts about 97 per cent of the acid into the di-sodium salt. One hundred grams of methyl sulphate are added in small portions with constant shaking, keeping the temperature below 40°. When the methyl sulphate has disappeared, the solution is strongly acidified with hydrochloric acid and extracted with ether. The ether layer is separated, washed with water, and the ether removed by evaporation. The residue is heated for one hour on the water bath with an excess of lime water and filtered. The insoluble residue of calcium salicylate is repeatedly extracted with boiling water, and the combined filtrates acidified with hydrochloric acid. The methyl ether of salicylic acid is deposited upon cooling in large monoclinic plates. It should be recrystallized from water until ferric chloride shows no trace of salicylic acid. Its methyl ester is easily obtained with methyl alcohol and hydrogen chloride, and boils at 245-246°. This boiling point agrees with that found by Schreiner<sup>13</sup> and not with the lower value given by Fölsing.<sup>14</sup> The ester-ether was saponified, and the resulting acid identified as the methyl ether of salicylic acid. The absorption spectra of these two compounds in neutral alcohol solutions are identical. We have photographed them in the presence of 1 and 5 equivalents of sodium ethoxide. Under these conditions the absorption band heading  $1/\lambda=3440$  in the methyl ether of salicylic acid is shifted toward the shorter wave lengths to  $1/\lambda=3640$ , both concentrations of alkali giving practically identical results. The persistence of this band is, at the same time, reduced, and the incipient band in the benzene region of the spectrum is lost. It is to be noted that, while alkali causes a shift toward the red in the compounds previously discussed, the shift in this instance is in the opposite direction. The former shift is characteristic of enol-keto tautomerism, and is not shown when the labile hydrogen atom is replaced by an alkyl group,

<sup>13</sup> *Ann. Chem. Pharm.* (1879), 197, 1.

<sup>14</sup> *Ber. d. deutschen chem. Ges.* (1884), 17, 486.

while the latter may be an ionization phenomenon. Baly and Schaefer<sup>17</sup> have pointed out from a study of cinnamylideneacetic, cinnamylidene-malononic, and other acids that the addition of alkali decreases, while the addition of acids increases, the free affinity of the carbonyl group, and state that the natural deduction from this is that the more the substance is ionized the less the free affinity possessed by the carbonyl group.

The amount of free affinity of the carbonyl group is greatest when the acid is not ionized and least in the easily ionized sodium salt.

The absorption curve of the methyl ether of methyl salicylate is neither shifted nor altered in any way in the presence of alkali. This behavior is to be expected from a nonionizable compound of this type.

It is interesting to note that the absorption bands heading at  $1/\lambda=3440$  of phenol, *o*-cresol, and of *o*-hydroxybenzyl alcohol, all in presence of 5 equivalents of alkali, almost coincide with that of the methyl ether of salicylic acid in neutral solution and of the methyl ether of methyl salicylate, and further that these 5 curves all show an incipient band in the benzene region. It is evident that under these conditions the internal molecular vibrations of these compounds are remarkably similar. In phenol, *o*-cresol, and *o*-hydroxybenzyl alcohol, the enol-keto tautomerism exists without the modifying influence of the carbonyl group, and the absorption curves of these three compounds and of their methyl ethers are almost identical. The replacement of the hydroxylic hydrogen atom of these compounds by sodium is thus seen to produce much the same effect as the adjacent carbonyl group produces in their ethers.

#### SALICYLIC ACID AND METHYL SALICYLATE. FIG. 4

The absorption spectra of these compounds have been described by Hartley and Huntington<sup>18</sup> and Hartley,<sup>19</sup> but, for purposes of comparison with the other compounds described in this paper, we have photographed salicylic acid in alcohol, and its methyl ester<sup>20</sup> in neutral water and in alcohol solutions,

<sup>17</sup> *Journ. Chem. Soc. London* (1908), 93, 1808.

<sup>18</sup> *Loc. cit.*

<sup>19</sup> *Journ. Chem. Soc. London* (1888), 53, 641.

<sup>20</sup> Methyl salicylate was photographed in absolute alcohol solutions, and in aqueous solutions which contained sufficient alcohol to complete the solution. One-tenth molar solutions were made in 50 per cent alcohol, one-hundredth in 35 per cent alcohol, and one-thousand in 3.5 per cent alcohol.

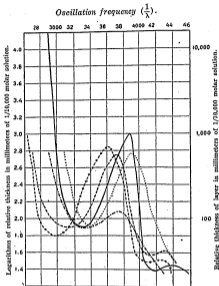


FIG. 4.—Full curve—salicylic acid and methyl salicylate.

Dash curve—methyl salicylate with 1 equivalent of sodium ethoxide.

Dot curve—salicylic acid with 5 equivalents of sodium ethoxide.

Dot and dash curve—salicylic acid with 300 equivalents of sodium ethoxide.

Dash and cross curve—methyl salicylate with 500 equivalents of sodium ethoxide.

salicylic acid in alcohol in the presence of 5 and 300 equivalents of sodium ethoxide, and methyl salicylate in alcohol in the presence of 1/10, 1, 3, and 500 equivalents of sodium ethoxide and in the presence of hydrogen chloride. We have observed that the curves obtained with water and with alcohol as the solvent are practically identical and in accord with data given by Hartley.

The activity of the carbonyl group of salicylic acid is reduced in the easily ionized sodium salt and also by the fixation of the labile hydrogen atom by methyl. This is shown in the charts of the absorption spectra both by a reduction in the persistence

of the absorption band of salicylic acid at  $1/\lambda=3300$  and by a shift of this band to  $1/\lambda=3400$ , a position which corresponds to the same band shown by salicylic acid in the presence of 5 equivalents of sodium ethoxide. In the latter case the salicylic acid is almost entirely in the form of the mono-sodium salt (the actual amount of the salicylic acid in the form of the di-sodium salt is about 11 per cent of the whole), and the shift to the shorter wave lengths may be due to the ionization phenomenon previously mentioned. With 300 equivalents of alkali, the salicylic acid in one-thousandth molar solution is approximately 9.2 per cent in the form of the mono-sodium salt and 90.8 per cent in the form of the di-sodium salt for  $n \times s/0.03=d$  where

$n$ =concentration of the free base,

$s$ =concentration of the mono-sodium salt,

$d$ =concentration of the di-sodium salt.

These values are computed for aqueous solutions since the hydrolysis constant in alcohol is not available. We believe the error thus introduced has no bearing on the general considerations.<sup>21</sup>

The absorption curve under these conditions is, therefore, that of di-sodium salicylate. The absorption band is much broadened; and the shift toward the shorter wave lengths, found in the presence of 5 equivalents of alkali, is more than counter-balanced by the shift toward the red which is characteristic of the enol-keto tautomerism. Since this absorption band has almost entirely disappeared, it is evident that the free affinity of the carbonyl group is approaching a minimum.

The curve for methyl salicylate in the presence of a small quantity of alkali, 1 equivalent, shows a shift toward the red and a decrease in the persistence of the large absorption band. In the presence of greater excess of alkali, the shift toward the red is increased, while no further reduction in the persistence is to be noted. The presence of acid causes no appreciable change in the absorption spectrum of methyl salicylate. Since the ionization constant of this compound<sup>22</sup> is very small; namely,  $1.2 \times 10^{-11}$ , it appears probable that no measurable effect is to be expected. All of the curves which have any significance are plotted in fig. 4.

<sup>21</sup> In one-thousandth molar alcohol solutions the addition of 10 per cent of water was necessary to keep the salts in solution.

<sup>22</sup> *This Journal*, Sec. A (1913), 8, 1.

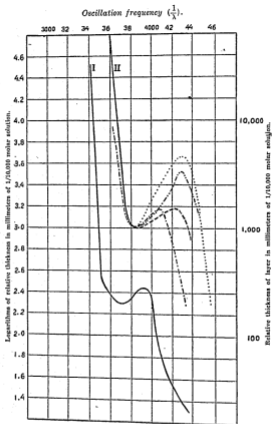


FIG. 5.—Curve I=methyl benzoate.  
 Curve II and dot curve=benzyl alcohol.  
 Curve II and dash-two-dot curve=benzyl acetate.  
 Curve II and dash curve=benzyl methyl ether.  
 Dash-dot curve=benzyl chloride.

BENZYL ALCOHOL, BENZYL ACETATE, BENZYL METHYL ETHER,  
BENZYL CHLORIDE, AND METHYL BENZOATE. FIG. 5

The absorption spectra of benzyl alcohol and benzyl ethyl ether have been studied by Baly and Collie,<sup>22</sup> and since it did not seem probable that the absorption band at  $1/\lambda=3600$  was correctly ascribed to this type of compounds by these authors and also for the reasons given above, we have included a study of benzyl alcohol and 4 closely related compounds in this investigation. Benzyl alcohol, acetate, methyl ether, and chloride were dissolved in pure ethyl ether and shaken repeatedly with dilute aqueous alkali, and then with water until neutral. The ether layer was dried with anhydrous copper sulphate, the ether evaporated, and the residue fractioned several times under reduced pressure. This procedure was found necessary to obtain pure compounds. The substances thus prepared show only one absorption band which lies in the benzene region of the spectrum and heads at  $1/\lambda=3850$  in each case. The persistence of this band decreases in these compounds in the order in which they are mentioned from the maximum shown by benzyl alcohol. From log. 3.0 to 4.8, and  $1/\lambda=3600$  to 3850, the curves of the first three compounds are identical while that of benzyl chloride apparently shows slightly greater general absorption. The divergence in the curve of the latter may be due to traces of impurities. No indication of an absorption band in this region of the spectrum is shown by any of these compounds. There is no doubt that their true absorption spectra bear little resemblance to the descriptions of Baly and Collie. Absorption bands outside of the benzene region of the spectrum are not to be expected in compounds of this type.

The absorption curve of methyl benzoate is very similar to those of the benzyl derivatives, but appears at greater dilution, and the absorption band heads nearer the visible region of the spectrum; namely at  $1/\lambda=3700$ . The absorption spectrum of the free acid has been described by Hartley and Huntington,<sup>24</sup> and it shows no noteworthy differences from that of methyl benzoate.<sup>25</sup>

<sup>22</sup> *Journ. Chem. Soc. London* (1905), 87, 1343.

<sup>23</sup> *Loc. cit.*

<sup>24</sup> Baly and Collie (*loc. cit.*) state: "The spectrum of benzoic acid has been observed by Hartley and Huntington, and only shows general absorption rather strongly. This is only to be expected from the presence of the ketonic oxygen in the  $\beta$ -position," a statement which does not seem to be strictly in accord with the facts.



## ILLUSTRATIONS

### TEXT FIGURES

- FIG. 1. Dash curve = phenol.  
Dot curve = phenol with 1/10 equivalent of sodium ethoxide.  
Full curve = phenol with 5 equivalents of sodium ethoxide.
2. Full curve = *o*-cresol in alcohol.  
Dot curve = *o*-cresol with 1 equivalent of sodium ethoxide.  
Dash curve = *o*-cresol with 5 equivalents of sodium ethoxide.  
Dash and dot curve = *o*-cresol in aqueous solution with 5 equivalents of sodium hydroxide.
3. Dot and dash curve = *o*-hydroxybenzyl alcohol.  
Dot curve = *o*-hydroxybenzyl alcohol with 5 equivalents of sodium ethoxide.  
Full curve = methyl ether of salicylic acid and methyl ether of methyl salicylate.  
Dash curve = methyl ether of salicylic acid with 5 equivalents of sodium ethoxide.
4. Full curve = salicylic acid and methyl salicylate.  
Dash curve = methyl salicylate with 1 equivalent of sodium ethoxide.  
Dot curve = salicylic acid with 5 equivalents of sodium ethoxide.  
Dot and dash curve = salicylic acid with 300 equivalents of sodium ethoxide.  
Dash and cross curve = methyl salicylate with 500 equivalents of sodium ethoxide.
5. Curve I = methyl benzoate.  
Curve II and dot curve = benzyl alcohol.  
Curve II and dash-two-dot curve = benzyl acetate.  
Curve II and dash curve = benzyl methyl ether.  
Dash-dot curve = benzyl chloride.